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**Finding a Single Molecule in a Haystack: Laser Spectroscopy of  
Solids from  $\sqrt{N}$  to  $N = 1$**

by

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**Finding a single molecule in a haystack:  
Laser spectroscopy of solids from  $\sqrt{N}$  to  $N = 1$**

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ABSTRACT

Single-absorber optical spectroscopy in solids may be regarded as the problem of finding a single dopant impurity molecule in a "haystack" composed of  $10^{12} - 10^{18}$  background host molecules and up to  $\sim 10^6$  additional impurity molecules. Detailed studies of the low-temperature inhomogeneously broadened  $0-0 S_1 \leftarrow S_0$  electronic transition of pentacene dopant molecules in *p*-terphenyl crystals have yielded both (1) observations of spectral structure scaling as  $\sqrt{N}$ , where  $N$  is the number of impurity molecules in resonance, and (2) the optical absorption spectrum of a single impurity molecule in a solid ( $N = 1$ ). Recent advances in fluorescence excitation of very small volumes have greatly improved the signal-to-noise ratio for a single molecule.

1. INTRODUCTION

Recent progress in the optical detection and spectroscopy of single ions in vacuum confined in electromagnetic traps has led to novel measurements that further our understanding of quantum physics. For example, various workers have achieved direct measurement of quantum jumps, Doppler sidebands, and other fundamental phenomena such as ion crystallization for ions in vacuum trapped by electromagnetic fields. By using laser-induced fluorescence and a novel hydrodynamically-focused flow to confine the molecules and reduce the scattering volume, single molecules of the protein B-phycoerythrin with the equivalent of 25 rhodamine 6G chromophores have also been detected. In contrast to the far-field optical approach, recent advances with various near-field spectroscopies such as scanning tunnelling microscopy (STM) have provided images of single molecules of benzene and CO on Rh surfaces and images of liquid crystal molecules on graphite to name a few examples.

*molecular* 25 \*Spectroscopy, \*Optical detection\*

The analogous problem of detection and spectroscopy of a single impurity absorber in a solid (called in the case of a molecular absorber, single-molecule detection, or SMD) would provide a useful tool for the study of local host-absorber interactions where the absorbing center is essentially at rest, confined by the host lattice, and where the normal averaging over many "equivalent" centers is removed. Compared to the other single-absorber experiments, SMD in solids provides a different set of experimental challenges. The problem can be likened to "finding a needle in a haystack", because unlike the ion-trap experiments, for example, the molecule of interest is hidden deep within a solid containing a large number ( $\approx 10^{12} - 10^{18}$ ) of "non-absorbing", potentially interfering host molecules within the laser focal volume. For example, if laser-induced fluorescence excitation were used for SMD and the host molecules had appreciable Raman (or Rayleigh) scattering cross sections, the signal from the one absorbing molecule could be swamped by the scattering signal from



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the host. Although this paper focuses on molecular impurity centers, the physical concepts apply equally well to ions, color centers, and other defect absorptions in solids.

Except in the case of an extremely special sample with only one impurity present in the laser focal volume, in normal samples there is in addition to the haystack provided by the host, a second interfering haystack: the other impurity molecules also present in the laser focal volume. Generally, at liquid helium temperatures, absorbing impurity (guest) centers in solids with zero-phonon transitions form inhomogeneously broadened lines,<sup>8</sup> where the overall line profile is caused by a (usually Gaussian) distribution of center frequencies for the individual absorbers that is broader than the (usually Lorentzian) homogeneous lineshape of the individual absorbers. The distribution of center frequencies is caused by dislocations, point defects, or random internal electric and strain fields and field gradients in the host material. This inhomogeneous broadening effect is strongest at low temperatures, because the homogeneous zero-phonon lines become much narrower than the inhomogeneous distribution only when the host phonons are quenched.

As an important first step toward SMD, it was necessary to begin by taking a very detailed look at the inhomogeneously broadened optical absorption line of a defect in a solid with large numbers of absorbers. In this regime, an unusual effect called statistical fine structure (SFS) was observed for the first time<sup>9,10</sup>. SFS results from (static) number fluctuations in the spectral density of absorbers with optical wavelength, and therefore scales as the square root of the number of absorbers in resonance. The observations of SFS will be described in Section 2 of this paper. Central to these measurements was the use of a powerful zero-background laser technique called frequency-modulation spectroscopy (FMS), first described by Bjorklund<sup>11</sup> in 1980.

With a firm understanding of SFS in inhomogeneous lines, it became possible to approach the ultimate limit of single center detection and spectroscopy, SMD. One reason for studying single absorbers rather than a large number of absorbers at the same frequency is the fact that for an inhomogeneously broadened line, the various centers located within a homogeneous width of a given laser frequency are located at that particular spectral position for a variety of possible reasons in general. This intrinsic multi-dimensional inhomogeneity cannot be removed with spectral hole-burning or coherent transient techniques. However, with SMD the absorption spectrum of an individual absorber can become directly accessible, as long as no other centers are present at the same frequency. This is a primary reason to pursue the spectroscopy of individual centers in condensed matter. Other motivations come from the fact that a single molecular impurity is a truly local probe of the minute details of a single local environment in a solid. The use of powerful spectroscopic methods as well as the properties of the inhomogeneous line itself make SMD feasible, and our successful SMD experiments<sup>12-14</sup> will be described in Section 3. With these observations, a new regime of optical spectroscopy may be envisioned in which some of the scientific advances and observations of physical effects made possible by the ion trap and STM techniques may be attempted in condensed matter.

## 2. SQUARE-ROOT SCALING: STATISTICAL FINE STRUCTURE

Due to the randomness associated with the imperfections in solid hosts, inhomogeneous absorption lines (at least near their centers) are often approximated by smooth, Gaussian profiles<sup>8</sup>. However, since the inhomogeneous line on a microscopic scale is simply a superposition of *discrete*

homogeneous lines with widths as much as 1000 times narrower than the overall inhomogeneous profile, the true shape of the inhomogeneous line cannot be a smooth function in reality. In fact, unavoidable number fluctuations in the density of absorbers per unit wavelength interval should give rise to a "spectral noise" on the overall Gaussian background that scales as the square root of the mean number of centers in resonance. To be precise, defining the average number of centers in the probed volume within one homogeneous width of the laser wavelength as  $\bar{N}_H$ , there should be a statistical fine structure (SFS) present on the absorption profile scaling in absolute magnitude as  $\sqrt{\bar{N}_H}$  (in the limit of  $\bar{N}_H \gg 1$ ). Since SFS arises from the absorption of many overlapping impurity absorptions, the absolute magnitude of the SFS is clearly larger than a single-molecule absorption signal (where  $\bar{N}_H \approx 1$ ). Therefore, observations of SFS would be expected to precede true single-molecule detection.

Recent observations of SFS for the model system composed of pentacene in *p*-terphenyl crystals at 1.5K provided a crucial first step toward single-molecule detection and spectroscopy<sup>9,10</sup>. This was achieved using the high-resolution and high-sensitivity technique of laser frequency-modulation spectroscopy (FMS)<sup>11</sup> to probe the optical absorption in a zero-background manner sensitive only to narrow spectral features.

Since its source is a random process, the SFS spectral structure changes for different probe volumes, and an "SFS landscape" of the inhomogeneous line can be generated by acquiring SFS spectra as a function of laser spot position, as in Figure 1. The bumps and valleys in this figure may be regarded as the "fuzz" on the top of the "haystack" represented by the pentacene inhomogeneous line that results from the statistics of independent, additive random variables. We note in passing that a crucial physical parameter may be derived directly from SFS measurements: by computing the autocorrelation of the measured spectra<sup>10</sup>, the homogeneous width of the underlying Lorentzian profiles may be determined.

Subsequent to the first observations of SFS, other researchers moved closer to single-absorber detection in solids by observing SFS at increasingly lower impurity concentrations. Lange et al.<sup>15</sup> relied upon fluorescence excitation of  $\text{Sm}^{2+}$  ions in  $\text{CaF}_2$  at 77K with a fixed frequency laser in tightly focused spots. These researchers saw Poisson fluctuations in the detected fluorescence as a function of the position of the focal spot and concluded that they had reached the level  $\bar{N}_H = 5$ . Another novel approach, developed by the Yen group at the University of Georgia<sup>16</sup>, used laser fluorescence excitation in a glass fiber doped with  $\text{Nd}^{3+}$  ions. Here the fiber geometry effectively maintains a small focus and a small probing volume in order to reduce background signals from the host. The measured SFS led these researchers to conclude that they had reached  $\bar{N}_H$  values on the order of a few tens of ions. In both cases, special detection geometries were necessary to avoid host background fluorescence.

### 3. FIRST OBSERVATIONS AT $N=1$ USING ABSORPTION SPECTROSCOPY

The first successful achievement of SMD,<sup>12</sup> done in the pentacene in *p*-terphenyl system, avoided the problem of fluorescence background from the host haystack by using a powerful zero-background absorption technique, laser FM spectroscopy (FMS)<sup>11</sup>. In brief, the optical absorption is measured using a phase-modulated light beam and a high-speed detector/rf lock-in combination sensitive only to amplitude modulation at the rf modulation frequency. The method operates by

using narrow spectral features in the sample to convert the frequency modulated light beam into an amplitude modulated beam, which after detection produces a signal at the output of the rf lock-in. Since the method directly senses the conversion of FM into  $\Delta M$ , any residual AM (also called RAM) from imperfections in the modulator can give rise to a spurious background signal. To overcome this, a secondary modulation of the spectral feature itself was implemented using Stark (or separately, ultrasonic) fields.

The size of the expected absorption signal from a single molecule is straightforward to estimate<sup>12</sup>. The change in absorbance,  $(\Delta\alpha)L$ , is given by the probability of absorption of a photon in the incident beam by the molecule,  $\sigma/\Lambda$ , where  $\sigma$  is the peak absorption cross section and  $\Lambda$  is the area of the laser beam. Clearly, then, one would prefer tightly focused laser spots and molecules with strong absorptions. In the first experiments, the focal spot was  $\approx 3 \mu\text{m}$  in diameter, and the peak (low-temperature) absorption cross section for pentacene is  $9.3 \times 10^{-12} \text{cm}^2$ , yielding an absorbance change of  $\approx 10^{-4}$ . This is not an extremely small signal except that detection must be performed with a light intensity that does not produce extreme power broadening. To meet this constraint in a tightly focused spot, the measurements were performed with only  $0.1 \mu\text{W}$  of light at the detector, which is an extremely small laser power for FMS. Such a low light level required an avalanche photodiode to avoid detector Johnson noise resulting in detection approximately 3 dB above the quantum limit.

In spite of these limitations, the FM/Stark and FM/US methods can be used to detect the optical absorption of a single molecule of pentacene in a solid crystal of *p*-terphenyl. Figure 2 shows examples of the spectra for the FM/Stark case. The first three traces show simulations to explain the expected single-molecule lineshape for either Stark or ultrasonic double modulation. Trace 2(a) shows a Lorentzian absorption profile of width  $\gamma$ , and trace 2(b) shows the expected simple FM signal<sup>17</sup>: two copies of the absorption line with opposite sign, spaced by  $2\nu_m = 150 \text{MHz}$  (in the limit  $\gamma \ll \nu_m$ , where  $\nu_m$  is the rf modulating frequency). With secondary modulation that causes frequency shifts less than the linewidth, the resulting double-modulation lineshape is the derivative of the simple FM lineshape (trace 2(c)). Thus the signature of a single molecule is a "W"-shaped feature with a large negative slope and a large positive slope separated by  $2\nu_m$ .

In a typical experiment, the laser frequency was set near the center of the inhomogeneous line, and the resulting strong SFS signal was used to optimize the optical and electronic configuration. Then as the laser wavelength was moved out into the wings of the line, the SFS amplitude dropped uniformly. Eventually spectra that appear to be superpositions of 2-5 single-molecule spectra like trace 2(c) were observed. Finally, sufficiently far out into the wings of the line, true single-molecule spectra could be recorded. Trace 2(d) shows a set of eight FM/Stark double modulation spectra of a strong in-focus molecule far out in the long-wavelength edge of  $O_1$ , along with several unavoidable weak repeatable features from out-of-focus molecules at the left and right edges of the laser scan range. These out-of-focus features were caused by molecules not located at the laser waist position. The fiducial bar marks a spectral range equal to  $2\nu_m$ . Trace 2(e) shows the average of the eight scans in 2(d), along with a fit to the central feature generated by a simple model for the double-modulation process<sup>14</sup>. The fit to the essential features of the SMD lineshape is reasonable, and the homogeneous width required by the fitting process is somewhat larger than the low-power homogeneous width, as expected.

Trace 2(f) shows the detected signal from a laser wavelength so far away from the pentacene site origins that no molecules are expected to lie in the laser scan range; this is the background shot and avalanche noise. In samples of undoped pure *p*-terphenyl, only a baseline noise level similar to the off-line data in Fig. 2(f) was observed, even near the center of the inhomogeneous line. Trace 2(g) shows spectra of the strong SFS observed near the center of the inhomogeneous line using a smaller number of averages. This spectrum is composed of a superposition of many "W" profiles like Figure 2(d) with many different center frequencies, illustrating the qualitative difference between spectra of large numbers of molecules (Fig. 2(g)) and spectra of one molecule (Fig. 2(d)).

Using the related FM/US technique,<sup>12, 14</sup> when the modulating frequency  $\nu_m$  is varied, the single-molecule lineshapes can be observed to expand and contract as required to maintain the proper spacing between the inner edges of the "W". Such clear variations in the recorded spectrum cannot be observed when many molecules are present in the laser scan. This, in conjunction with the shape of the observed features, the position relative to the pentacene in *p*-terphenyl origins, the lack of such signals in undoped samples, and the appearance of single-molecule spectra with both the FM/Stark and FM/US techniques, leads us to the conclusion that the recorded spectra are due to single molecules of pentacene. However, in both cases, the signal-to-noise ratio (SNR) was only approximately 3-5, and further improvements in this SNR proved difficult since the measurements were already performed near the quantum limit and power broadening was already present.

#### 4. RECENT ADVANCES IN SMD USING FLUORESCENCE EXCITATION

As a result of the aforementioned demonstrations that the pentacene in *p*-terphenyl system is well-suited for single-molecule experiments, the group of Orrit *et al.* have recently utilized fluorescence excitation techniques to acquire single-molecule spectra<sup>18</sup>. To achieve this, extremely small excitation volumes available from sublimed samples or optical fibers must be used, and the efficiency of fluorescence collection must be very high (N.A.  $\approx 1$ ). Orrit *et al.* were able to see clearly separated single-molecule peaks in the fluorescence excitation spectrum with higher signal-to-noise than was available from the FMS technique, at lower probing intensities.

As an example of the power of the fluorescence excitation technique, Figure 3 shows data for a  $\approx 10 \mu\text{m}$  thick, low concentration sublimed sample of pentacene in *p*-terphenyl at 1.5 K. To acquire these data, we excited the sample with 20 nW of laser power in a  $5 \mu\text{m}$  focal spot, collected the Stokes-shifted fluorescence passing through a long-pass filter with a N. A. 0.98 paraboloidal mirror immersed in the superfluid helium, and subsequently counted the photons detected by a GaAs phototube. Trace 3(a) shows the frequency region covering the central part of the inhomogeneous line for the  $O_1$  site at 592.321 nm. The structures appearing to be noise are not; they are direct measurements of the SFS statistical variations described in Section 2. This structure is static and repeatable and arises directly from statistical variations in the spectral-density of absorbers with laser frequency.

More interesting are the spectral features in the wings of the inhomogeneous line shown in Trace 3(b). At a detuning of -2.7 GHz, clearly resolved, individual single-molecule peaks can be observed. Similar single-molecule peaks are present on the blue edge of the inhomogeneous line. Indeed, at sufficiently low laser intensity ( $0.5 \text{ mW/cm}^2$ )<sup>19</sup>, the individual pentacene spectra reach the lifetime-limited width of  $7.8 \pm 0.2 \text{ MHz}$ .

Such high SNR's for single molecules have allowed the observation of one unexpected new physical effect so far: spectral diffusion of individual pentacene impurity molecules in a crystal at 1.5K<sup>20</sup>. To be more precise, we have found that two distinct classes of molecules are present: class I, which have center frequencies that are stable in time, and class II, which show spontaneous, discontinuous jumps in resonance frequency of 20-60 MHz on a 1-420 s time scale. The occurrence of class II defects is quite common in the wings of the inhomogeneous line (increasing to 40 % at +0.23 nm from line center), but only class I defects have been observed in a spectral region from 0.003 to 0.01 nm from line center, suggesting that disorder in the crystal is partially responsible for the spectral migration. Further, the jumping rate does not appear to depend upon the laser power used to measure the fluorescence excitation spectrum.

Since the resonance frequency of an impurity molecule in an inhomogeneously broadened line is extremely sensitive to the local strain at the position of the molecule, the spectral jumps appear to occur because the class II pentacene molecules are coupled to an (unidentified at present) ensemble of two-level systems in the host crystal undergoing phonon-assisted tunneling. One possible source for the tunneling transitions could be discrete librations of the central ring of the nearby *p*-terphenyl molecules about the *p*-terphenyl molecular axis, but further experiments are necessary to conclusively identify the molecular motions responsible for the effect. This surprising observation of spectral jumping is analogous to spectral diffusion processes that play a crucial role in the physics of glasses and other amorphous materials; here, the single-molecule technique allows the spectral changes to be followed in real time.

## 5. CONCLUSION

The attainment of single-molecule detection and spectroscopy in solids opens up a new frontier of single-absorber experiments in which the measured properties of the absorbing center are not averaged over many "equivalent" absorbers. Here the absorbing entity is exquisitely sensitive to the symmetry and perturbations introduced by the local environment such as the local vibrational modes and the true local fields. While as a general technique the method presented here may not be applicable to all molecular impurities, it can be applied to the large number of absorbing ions and molecules in solids that have zero-phonon transitions and strong absorptions, ideally with large fluorescence emission efficiency. The detectability of the resulting single-center signal for specific systems must be evaluated in each case. It is clear, however, that further information about specific local environments will be forthcoming in future experiments on single impurities in solids.

## 6. ACKNOWLEDGEMENTS

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Fig. 1. SFS structure versus laser spot position and laser frequency near the inhomogeneous line center for pentacene in *p*-terphenyl. A sequence of 100 spectra were obtained, moving the 20 $\mu$ m laser spot by 2 $\mu$ m after each spectrum, and the results plotted as a contour plot of the SFS signal to show the SFS "landscape". After Ref. 10.

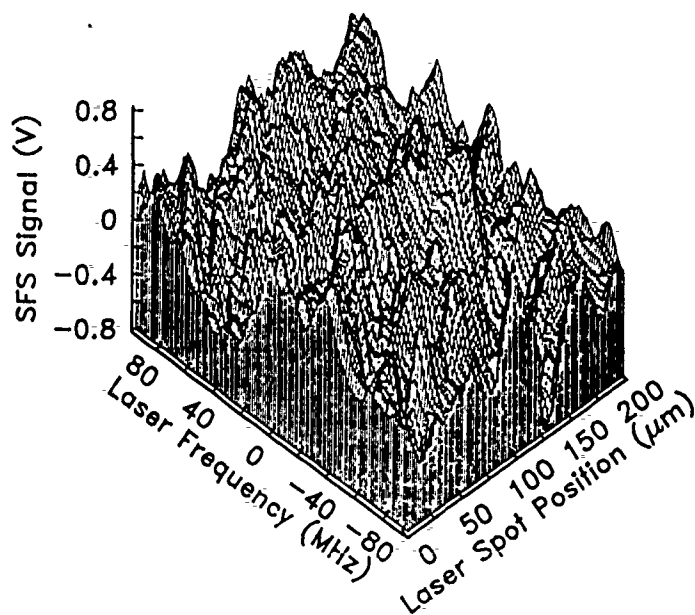


Fig. 2. Single-molecule spectra using FM/Stark technique (quadratic Stark effect) (a) Simulation of absorption line. (b) Simulation of FM spectrum for (a),  $\nu_m = 75$  MHz. (c) Simulation of FM/Stark double-modulation lineshape. (d) SMD spectra at 592.423 nm, 512 averages, 8 traces overlaid, bar shows value of  $2\nu_m = 150$  MHz. ( $O_1$  line center is at 592.326 nm.) (e) Average of traces in (d) with fit to the in-focus molecule (smooth curve). (f) Signal very far off line at 597.514 nm, same conditions. (g) Traces of SFS at the  $O_2$  line center, 592.186 nm, 128 averages each. After Ref. 12.

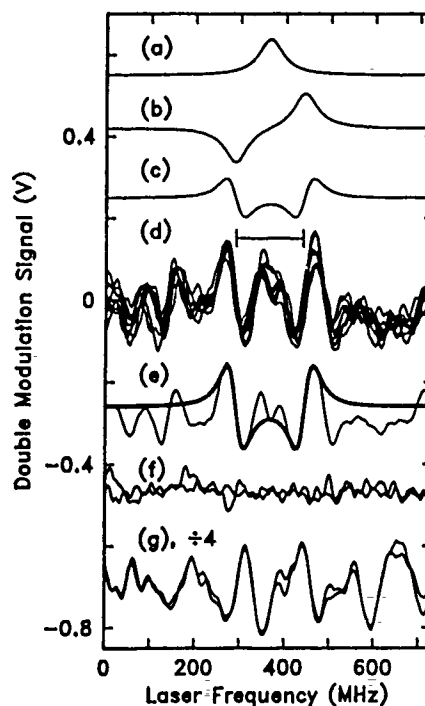
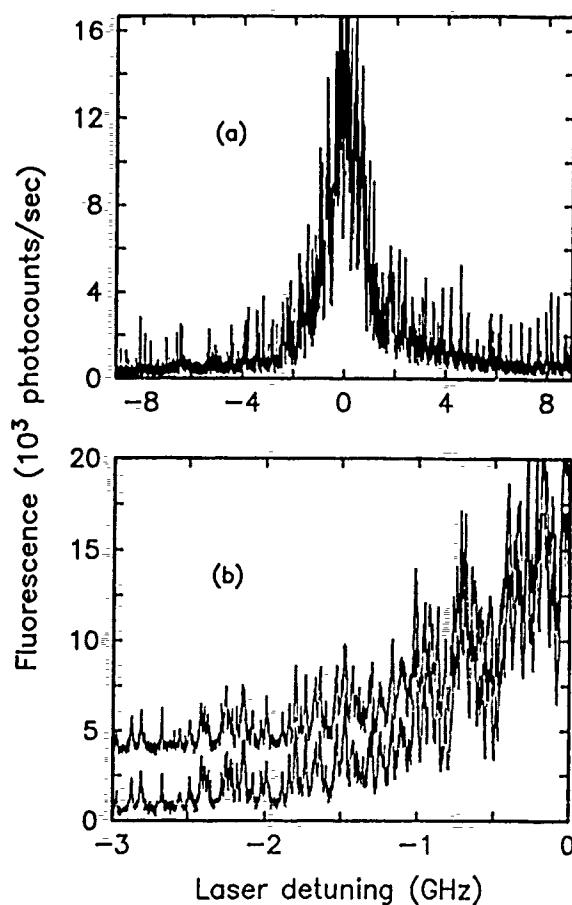


Fig. 3. Fluorescence excitation spectra for pentacene in a *p*-terphenyl crystal at 1.5 K near the  $O_1$  site origin. (a) Region near the center of the line. (b) expanded scale in the wing, showing individual single-molecule peaks.



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